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(54) **Method for preparing an emulsion of adjustable viscosity; the emulsion thus prepared and foodstuff obtained using such emulsion.**

- (57) Preparation of a heat-stable oil-in-water emulsion of adjustable viscosity by
- a) preparing an oil-in-water emulsion having an oil content of from 10 to 25 wt.% based on the total emulsion and a whey protein content of from 3 to 7 wt.% based on the total emulsion, the preparation of said emulsion including homogenization such that at least 85% of the fat particles present possess an average diameter smaller than 1.2  $\mu\text{m}$ , whereafter
  - b) the pH of this emulsion is adjusted to a value higher than 6.5 and subsequently
  - c) the emulsion is flow-heated at this pH for a period of 0.5-5 minutes at a temperature of 75-140 °C, whereafter
  - d) the emulsion is cooled to a temperature lower than 20 °C, whereafter, with stirring, the pH of the emulsion is adjusted to a value between 4 and 5, so that in the final product a permanent structure is obtained.

**EP 0 603 981 A1**

This invention relates to the preparation of a heat-stable oil-in-water emulsion of adjustable viscosity. The invention relates in particular to the preparation of slightly sour food products having a viscous character.

In the preparation of liquid foodstuffs, the structure or consistency is an important parameter in connection with the organoleptic sensation.

Besides the taste, this consistency, typically also referred to as viscosity and/or firmness, determines the perception of a foodstuff to a considerable extent.

The structure is mainly determined by the interaction between the different constituents and in particular that with water. The extent to which the water present can be bound is determinative of the height of the viscosity.

In general, to obtain a desired structure, a thickening or gelling agent is added to the aqueous foodstuff. Examples of such thickening agents which, even in a minor concentration, are capable of binding much water and hence of structuring an aqueous foodstuff, are polysaccharides such as gums, starches and carrageenans. Accordingly, in the preparation of sour products such as dressings, it is in particular starch and gums that are used as thickening agents.

However, these polysaccharides lack the ability to stabilize a dispersion of fat or oil in water, i.e., they are not emulsifiers.

In contrast with these polysaccharides, protein, such as egg albumin, has both gelling and emulsifying properties. Because chicken protein is relatively expensive and has good functional properties only in fresh condition, other, cheaper protein sources were looked for.

This investigation was focused in particular on the applicability of whey proteins both as emulsifier and as thickener, the attention being directed in particular to the replacement of egg yolk as emulsifier in the preparation of mayonnaise-like products.

U.S. Patent No. 3,892,873, for example, discloses the preparation of dressings and mayonnaise with an oil content of at least 40%, wherein partly thermally denatured whey proteins are used as emulsifier and thickener. The thermal denaturation of the whey proteins involves at least 70% denaturation. Because the emulsifying properties of denatured protein are less good, products thus prepared have the drawback of a less good stability, in particular the emulsion stability.

Dutch patent specification 181,326 discloses the application of thermally modified and desalted whey proteins as emulsifier and structure former in a yoghurt-like dressing. Because the whey proteins were heated at slightly increased pH, they were indeed denatured, but remained soluble. This method, too, leads to a product of less good stability.

European patent specification 52 899 discloses a method for preparing a spread of low fat content in the form of a water-in-oil emulsion. Here, in addition to whey proteins, thickeners are used as well.

A more recent application of whey proteins as emulsifier in the preparation of oil-in-water emulsions is described in U.S. Patent No. 4,720,390, which relates to the preparation of a gelled product which can be used as ingredient for pancakes and desserts. According to the method described, an emulsion of a protein content in the range of 4-12 wt.% and an oil content in the range of 2-40 wt.%, wherein the average dimensions of the fat particles are between 0.1 and 6  $\mu\text{m}$ , are batchwise heated at a pH between 3.5 and 8.

A major limitation of this method is that it is only applicable to end products, so that a flowing, continuous process operation cannot be employed in the preparation. The reason for this is that under the influence of relatively high shearing forces the structure obtained is irreversibly damaged, so that it is impossible to mix other constituents into the product once it has been structured.

The object of the present method is to provide a method by the use of which in a continuous process operation, stable and heat-resistant emulsions are obtained, which at a slightly acidic pH value yield structures whose viscosity is adjustable within certain limits.

According to the invention, a heat-stable emulsion of adjustable viscosity is obtained by carrying out the following process steps.

As starting product, an oil-in-water emulsion is prepared having an oil content in the range of 10-25 wt.% based on the total emulsion and a whey protein content in the range of 3-7 wt.% likewise based on the total emulsion. The preparation of this emulsion includes homogenization such that at least 85% of the fat particles present possess an average diameter less than 1.2  $\mu\text{m}$ , as determined with a Malvern PSA 2600. For this purpose, preferably a homogenization pressure higher than 25 MPa is used.

Then the pH of this emulsion is adjusted to a value higher than 6.5 and preferably to a value between 6.5 and 8.0, whereafter the emulsion is heated while flowing (this treatment is also referred to hereinafter as 'flow-heating') at this pH for a period of 0.5-5 minutes at a temperature of 75-140 °C. Preferably used for this purpose is a heating system with a high heating rate in the range above 75 °C and in particular a direct heating system (DSI). This heating leads to a denaturation of the whey proteins but not to heat instability

and hence not to flocculation, for instance.

Then the emulsion "activated" by the preceding treatments is cooled to a temperature below 20 °C, preferably below 10 °C, whereafter, with stirring, the pH thereof is adjusted to a value between 4 and 5, so that in the final product a permanent structure is obtained. For adjusting this pH value, any known nutrient  
5 acid, such as for instance lactic acid, can be employed.

If, for instance, a WPC of an ash/protein ratio between 0.10 and 0.20 (WPC-50 and WPC-35, respectively) is used for preparing an emulsion comprising a maximum of 20% fat, while, for obtaining optimum heat stability a maximum protein content of 5% is used, the structure can be provided in a suitable manner by adjusting the pH of the emulsion to a value between 4 and 4.5 by adding a solution of a  
10 nutrient acid to the emulsion under stirring conditions.

If a WPC of an ash/protein ratio between 0.03 and 0.10 is used, an emulsion of a higher whey protein content, for instance up to 7%, can be prepared without any objection. In the case of such an emulsion, after the heating step the structure can be provided in a suitable manner by aseptically dosing a NaCl solution to the "activated" emulsion until an ash/protein ratio of 0.20 or higher is attained, and thereafter or  
15 simultaneously the pH is adjusted to a value between 4 and 5.

If desired, the dosing of the acid can be performed aseptically by in-line injection and mixture.

By virtue of the structure formed in the product obtained, it acquires a high-viscous to paste-like consistency, which, depending on the protein/fat ratio, the pH and the ash content of the protein, is adjustable within certain limits, as will be demonstrated in the examples hereinafter. The structure formed  
20 has a thixotropic character; it loses apparent viscosity with stirring (shear) and the viscosity decreases more strongly with increasing shear. The viscosity lost is restored after the shear is removed. In spite of the shear, the product obtained retains a homogeneous and smooth character; no visible syneresis occurs. For this reason, the product obtained can be mixed with other constituents, such as aromatic substances, vegetable and fruit constituents, etc., without loss of the smooth, homogeneous structure.

By virtue of its continuous character, the method according to the invention is so flexible that it is possible to prepare not only end products such as foodstuffs, but also semimanufactured products, such as base materials for the preparation of pharmaceuticals, for instance ointments, etc.

Surprisingly, it has been found that the heat stability of the whey proteins in the emulsion prepared by the method according to the invention is such that this emulsion, even at relatively high protein contents,  
30 can be heated to temperatures above 75 °C without the system becoming macroscopically unstable. Partly as a consequence of this, it is possible to obtain the emulsion in powder form, for instance by spray-drying.

For the purpose of processing the heated emulsion into an emulsion powder which after reconstitution has a desired viscosity, a dry acidifying agent is generally added to the powder. Thus, when, for instance, the starting material is a whey protein concentrate which has an ash to protein ratio of between 0.10 and  
35 0.20 and has been heated at a pH between 7 and 7.5 and subsequently been spray-dried, an acidifying agent in the form of glucono- $\delta$ -lactone or citric acid can be added, so that after reconstitution the pH of the product will be between 4.2 and 4.5.

The whey proteins used in the method according to the invention may have been prepared by a method that is known per se.

According to a suitable method of preparation, they are obtained by ultrafiltration of cheese whey, for instance. This ultrafiltration leads to a particular ratio of the protein content to the solid content and hence to a particular ratio of whey protein to ash. It is customary to characterize whey protein concentrates (WPC) thus obtained on the basis of the whey protein content, so that WPC-80, for instance, is a whey protein concentrate comprising 80% (undenatured) whey proteins.

The whey proteins can also be obtained, for instance, by desugaring cheese whey, optionally in combination with desalting through electrodialysis or ion exchange, until a protein content, based on the solids, of preferably at least 35% is achieved.

In the emulsion according to the invention, it is possible to use any fat or any oil, both vegetable and animal and mixtures thereof, as are known for the preparation of foodstuff emulsions, such as spreads and  
50 sauces.

The invention will now be further explained in and by the following experiments and examples.

### **Experiment 1**

To determine the heat stability of the emulsion according to the invention, the following experiment was carried out.

A dispersion of 3.5% whey proteins (A), prepared from a WPC-80 having an ash/protein ratio of 0.03, was adjusted to a pH value of 7.5 using a sodium hydroxide solution.

A similar type of whey protein concentrate, though with a protein concentration of 5.5% (B), was emulsified with 15% butter oil through homogenization at 30 MPa. The pH of this oil-in-water emulsion was likewise adjusted to a value of 7.5.

Under heating of a tubular heat exchanger, both preparations were heated at 85 °C for 5 minutes. Dispersion (A) appeared to be heat-unstable and this dispersion left the heater in highly flocculated condition. Emulsion (B), on the other hand, of which 4.4% whey protein is not present in the oil/water interface, appeared to be heat-stable and this emulsion left the heater as a homogeneous thin fluid.

## Experiment 2

This experiment was an investigation of the influence of the pH upon heating on the heat-stability on the one hand and on the extent of viscosity of an oil-in-water emulsion on the other.

A dispersion of whey proteins with 6.5% protein was homogenized at 300 bar with 15% butter oil, such that 5.5% whey protein was present in the emulsion, and portions of this emulsion were adjusted to different pH values. These portions were subsequently flow-heated on a laboratory heater for 5 minutes at 85 °C.

After the non-flocculated emulsion had cooled to a temperature of 10 °C, the pH thereof was adjusted to a value of 4.3 using lactic acid under stirring conditions. The structures formed were assessed for viscosity. This viscosity was measured with a rotary viscometer at a shearing rate of 227 s<sup>-1</sup>. The results of these measurements are summarized in Table 1 below.

Table 1

Heating pH	Heat-stability at heating pH	Viscosity (mPa.s) at pH 4.3
3.5	yes	10
4.0	no	n.m.
4.5	no	n.m.
6.5	no	n.m.
7.0	yes	60
7.5	yes	80

## Experiment 3

This experiment was an investigation of the influence of the salt content, expressed as the ash/protein ratio, on the heat stability and on the extent of structure formation at acid pH.

A 4.1% protein dispersion was prepared from whey protein products of different ash/protein ratios and it was homogenized with 15% butter oil at 25 MPa until such a distribution of the size of the fat globules in the emulsion was obtained that at least 85% of these particles possessed an average diameter smaller than 1.2 µm. The pH of these emulsions was adjusted to a value of 7.5 and the emulsions were subsequently flow-heated, as was indicated in Experiment 2.

After the preparations had cooled off and been acidified with lactic acid to a pH of 4.3, the viscosity was measured at 10 °C and a shearing rate of 129 s<sup>-1</sup>. The results are summarized in Table 2 below.

Table 2

Type of WPC	Ash/protein	Viscosity (mPa.s)	
		after heating	after acidification
WPC-80	0.03	6	25
WPC-60	0.07	8	400
WPC-80 + permeate	0.10	18	600
WPC-35	0.19	177	2000
WPC-80 + NaCl <sup>1)</sup>	0.20	6	120 <sup>3)</sup>
WPC-80 + NaCl <sup>2)</sup>	0.20	8	200 <sup>3)</sup>

<sup>1)</sup> NaCl added after heating of the emulsion

<sup>2)</sup> NaCl added prior to heating

<sup>3)</sup> This viscosity was determined at a shearing rate of 229 s<sup>-1</sup>.

#### Experiment 4

This experiment was an investigation of the influence of the fat content, given a constant protein content, on the viscosity.

A number of whey protein dispersions, having an ash/protein ratio of 0.20 and prepared using a WPC-35, were homogenized with a varying butter oil content at 25 MPa until in all cases a protein content of 3% was obtained in the emulsion.

The pH of the emulsions was adjusted to a value of 7.5 and the emulsions were flow-heated for 5 minutes at 90 °C using a tubular heat exchanger.

After cooling, the pH of the emulsions was slowly adjusted to a value of 4.5 using 10 g glucono- $\delta$ -lactone per kilogram product.

Using a rotary viscometer, the viscosity was measured at a shearing rate of 23 s<sup>-1</sup> and 10 °C, after the pH had acquired a value of 4.5.

The measured viscosities, in conjunction with the fat content, are summarized in Table 3 below.

Table 3

Fat content	Viscosity (mPa.s)
10	960
12	1200
15	1750
17	2300

#### Example 1

This example describes the preparation of a pasty slightly acid product using a continuous process operation.

Using a WPC-50 whey protein concentrate having an ash/protein ratio of 0.10, two oil-in-water emulsions were prepared, respectively containing 18 and 20% milk fat.

The emulsions respectively contained 5.5 and 4.5% protein and they were homogenized in two steps at 55 °C at pressures of 25 and 4 MPa, respectively.

By means of lye injections, the pH of the emulsions was adjusted to a value of 7.5 and using the direct UHT system (Sterilab Alfa Laval) the emulsions were heated to 130 °C, followed by prolonged heating for 30 seconds.

After the emulsions had cooled to 5 °C through a flash cooling and heat exchanger, they were subjected to in-line acidification with a 25% solution of lactic acid until the pH had attained a value of 4.3.

For the purpose of the acidification, the acid was injected by means of a displacement pump and subsequently the acid was mixed with a high-speed mixer arranged in line.

The pasty products obtained were aseptically charged to small containers. Prior and subsequent to heating, the emulsions were analyzed for fat globule size distribution ( $d_{vs}$ ) and after acidification they were analyzed for the extent of structure formation by measuring the firmness, determined using LFRA Stevens texture meter (cone  $\varnothing$  = 20 mm) (penetration depth = 20 mm).

Table 4

Product	$D_{vs}(\mu\text{m})$	Firmness at 10°C (g)
Emulsion 18% fat	< 1.2	$\leq 10$
Emulsion 20% fat	< 1.27	$\leq 10$
After heating 18% fat	1.9	$\leq 10$
After heating 20% fat	2.2	$\leq 10$
After acidification 18% fat	n.m.	300
After acidification 20% fat	n.m.	400

### Example 2

In this Example the pulverization of an activated whey protein emulsion is described.

Using a two-stage homogenization at pressures of 250 and 40 bar, respectively, and 55 °C, an emulsion containing 20% milk fat was prepared. The emulsion was prepared using a WPC-60 whey protein concentrate having an ash/protein ratio of 0.07. The protein content of the emulsion was adjusted to 4%.

With vigorous stirring, the pH of a portion of the heated emulsion was adjusted to a value of 6, whereafter 15% maltodextrin was dissolved (powder B). This mixture as well as another portion of the emulsion of a pH of 7.2 (powder A) were subsequently dried via a two-stage dryer with a nozzle atomizer.

The air inlet and outlet temperatures were set at 80 °C and 180 °C, respectively. The temperature range of the fluid bed was 60, 40 and 20 °C.

The two emulsion powders were subsequently characterized on the basis of reconstitution and structure forming properties at a pH of 4.3, and further the two powders were compared with the non-dried product. The results are summarized in the following table.

Table 5

Variant	Solubility	Structuring ability
powder A	poor <sup>1)</sup>	moderate to poor
powder B	good <sup>2)</sup>	good
liquid	good	good
powder A + 0.5 DTT <sup>3)</sup>	good	good

<sup>1)</sup> The agglomerates of fat globules with whey proteins do not dissolve in water.

<sup>2)</sup> After dissolution the fat globules appear to be finely distributed; a few small agglomerates.

<sup>3)</sup> By drying the activated emulsion at an increased pH the fat globules covered by whey proteins agglomerate by way of sulfur bridges. Di-thiothreitol (DTT) is a reducing agent which specifically breaks these disulfide compounds.

### Claims

1. A method for preparing an oil-in-water emulsion, characterized in that a heat-stable emulsion of adjustable viscosity is obtained by
  - a) preparing an oil-in-water emulsion having an oil content of from 10 to 25 wt.% based on the total emulsion and a whey protein content of from 3 to 7 wt.% based on the total emulsion, the preparation of said emulsion including homogenization such that at least 85% of the fat particles

present possess an average diameter smaller than 1.2  $\mu\text{m}$ , whereafter

b) the pH of this emulsion is adjusted to a value higher than 6.5 and subsequently

c) the emulsion is flow-heated at this pH for a period of 0.5-5 minutes at a temperature of 75-140 °C, whereafter

5 d) the emulsion is cooled to a temperature lower than 20 °C, whereafter, with stirring, the pH of the emulsion is adjusted to a value between 4 and 5, so that in the final product a permanent structure is obtained.

10 2. A method according to claim 1c, characterized in that the product obtained is subsequently dried.

3. A method according to claim 1, characterized in that the pH mentioned in step b) of said claim is adjusted to a value between 6.5 and 8.0.

15 4. A method according to claim 1, characterized in that the heating step described in step c) of said claim is carried out in such a manner that the temperature of 75 °C-140 °C is attained as fast as possible.

5. A method according to claim 4, characterized in that for the purpose of heating a direct heating system (DSI) is used.

20 6. A method according to claim 1, characterized in that step d) comprises cooling to a temperature lower than 10 °C.

7. An emulsion obtained by the use the method according to one or more of claims 1-6.

25 8. A foodstuff containing the emulsion according to claim 7.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 93 20 3642

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	EP-A-0 485 663 (QUEST INTERNATIONAL) * page 3, line 27 - line 30 * * page 3, line 35 * * page 4, line 15 - line 29 * zie samenvatting * claims 1-4,12-17; examples 6,8 * ---	1-8	A23L1/24 A23D7/02 A23L1/19
A	EP-A-0 195 365 (NESTLE) * claims 1-10 * * examples *	1-8	
D	& US-A-4 720 390 (...) ---		
A	EP-A-0 076 549 (UNILEVER) * page 2, line 16 - line 31; claims; example 1 * * page 3, line 20 - line 32 * ---	1-8	
A	EP-A-0 129 346 (LAND O'LAKES) * claims 1-3,9,11-33 * * page 8, line 9-18 * ---	1-8	
D,A	EP-A-0 052 899 (UNILEVER) * claims 1,7 * * page 1, line 8 - line 20 * * page 3, line 13 - line 15 * * page 3, line 7-11 * ---	1-8	TECHNICAL FIELDS SEARCHED (Int.Cl.5)  A23L A23D A61K
A	GB-A-2 229 077 (KRAFT EUROPE R& D) * claims 1,2,4,5,7,9,12-14 * * page 2, line 15 - page 3, line 6 * ---	1-8	
A	GB-A-2 063 273 (STICHTING BEDRIJVEN VAN HET NEDERLANDS INSTITUUT VOOR ZUIVELONDERZOEK) * claims; examples II,III * & NL-C-181 326 (...) ---	1-8	
D			
-/--			
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>7 March 1994</b>	Examiner <b>Van Moer, A</b>
<b>CATEGORY OF CITED DOCUMENTS</b>  X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			





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Application Number  
EP 93 20 3642

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
D,A	US-A-3 892 873 (E.P.KOLEN ET AL.) * claims; examples * -----	1-8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 7 March 1994	Examiner Van Moer, A
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			